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METHODS FOR POLYMERIZATION OF ELECTRONIC AND PHOTONIC POLYMERS

CROSS-REFERENCE TO RELATED APPLICATIONS

This is a continuation-in-part of U.S. Application Serial No. 09/994,998, filed November 27, 2001, in the names of Sukaut Tripathy, et al, which, in turn, claims the benefit of U.S. Provisional Application No. 60/253,109, filed November 27, 2000, both of which are hereby incorporated herein by reference.

STATEMENT OF GOVERNMENT INTEREST

The invention described herein may be manufactured and used by the U.S. Government for governmental purposes without the payment of any royalty thereon.

BACKGROUND OF THE INVENTION

Recently, there has been an increased interest in tailored development of polyaromatic polymers, particularly polyaromatic polymers that are electrically conductive and/or have useful optical properties. Examples of electrically conductive polymers include certain polyanilines, polythiophenes, polypyrroles, and polyphenols. These conductive polyaromatic polymers may be used in a variety of electronic devices, including electro-chromic

devices, light-emitting diodes, electrostatic discharge protection, and light weight batteries. Of these polyaromatic polymers, polyanilines are the most extensively studied, due largely to superior electrical properties, such as high discharge capacity.

In addition to the above-named electrical properties, thermal and structural properties of polyphenols have long been exploited. In particular, phenol-formaldehyde resins, such as novolacs and resols, have found wide application as wood composites, laminates, foundry resins, abrasives, friction and molding materials, coatings and adhesives, fiber binders, and flame retardants. The use of formaldehyde in polyphenol synthesis, however, presents a significant toxicological and environmental hazard.

Despite the industrial utility of polyaromatic polymers, their synthesis remains problematic. Known difficulties in the synthesis of such polymers include inconsistent product composition, due in part to extensive branching of the polymers. In addition, many of the polyaromatic polymers are insoluble, or sparingly soluble, in common solvents, leading to poor processability. The use of toxic reagents, as noted above, is another undesirable feature of current synthetic methods. A search for new methods of synthesizing polyaromatic polymers has not heretofore yielded a commercially viable approach.

Many of the synthetic approaches to forming polyaromatic polymers use a heme-containing enzyme to catalyze the

polymerization. Any such catalyst must necessarily be stable and active under acidic conditions, as acidic conditions are required in order to synthesize an electrically conductive form of a polyaromatic polymer, such as polyaniline.

The increasing environmental problem of hazardous chemical wastes has led to an upsurge in efforts toward the development of biochemcial alternatives for synthesis of electronic and photonic polymers. Enzymatic polymerizations have attracted much attention with oxidative enzymes, such as horseradish peroxidase (HRP), being used for the synthesis of polyanilines and polyphenols through oxidative free radical coupling reactions.

Unfortunately, HRP and other peroxidases are inactive at low pH and are prohibitively expensive to use commercially. Hematin has been used to mimic the catalytic activity of HRP. However, despite its lower costs, hematin is a non-ideal catalyst for commercial polymerizations because of its low solubility in acidic, aqueous media. The low solubility of hematin under these conditions leads to an extremely low rate of polymerization and very poor yields.

The mechanism for HRP catalyzed polymerization involves the interaction of the heme-iron cofactor of the enzyme with the peroxide yielding an oxidized heme-iron complex. Subsequently, the oxidized heme-iron complex reacts with the substrate in a one-electron transfer reaction to produce the substrate radical and a

new iron-heme complex followed by the coupling of the radicals to form the polymer.

This enzymatic approach has not been extended to polythipophenes or polypyrroles, which have high electrical conductivity. This is because monomers, such as (3,4)-ethylenedioxythiophene (EDOT) and pyrrole (PYR), complexed with the active site of the enzyme catalyst cause deactivation of the latter and have proved to be unsuitable substrates for this enzymatic polymerization. This deactivation phenomenon drastically limits the prospects for the enzymatic synthesis of a wide range of polymers for possible industrial applications. The present invention evolved from exploration of the possibility of usage of a modified hydroxy ferriprotoporphyrin Hematin to serve as a catalytic center.

There is a need for a low cost, high efficiency means of synthesizing polyaromatic electronic and photonic polymers, which means is compatible with conditions required to synthesize polymers with commercially desirable properties.

SUMMARY OF THE INVENTION

The invention generally is directed to a derivatized hematin, to a method of forming assembled and derivatized hematins, and to methods for polymerizing an aromatic monomer with an assembled hematin or a derivatized hematin.

Accordingly, an object of the present invention is to provide a novel method for the synthesis of a conducting complex such as poly (3,4)-ethylenedioxythiophene/sulfonate polystyrene (PEDOT/SPS).

A further object of the present invention is to provide a novel method for the synthesis of a conducting complex of polypyrrol/sulfonate polystyrene (PPYR/SPS).

A further object of the present invention is to provide a novel method for the synthesis of a conducting complex of copolymers PPYR-PEDOT/SPS.

A further object of the present invention is to provide a method which results in the production of copolymers Polyaniline-PPYR/SPS, which have electrical and chemical stability, and improved processability.

A still further object of the present invention is to provide a method which results in the production of copolymers Polyaniline-PEDOT/SPS which have electrical and chemical stability, and improved processability.

Still another object of the present invention is to provide a method which results in the production of copolymers Polyaniline-PEDOT-PPYR/SPS, which have electrical and chemical stability, and improved processability.

A still further object of the present invention is to provide a method which results in the synthesis of a Polyaniline-PPYR-PEDOT/SPS polymer complex wherein the optical and electronic

properties of the final complex can be tailored and optimized by judicious choice or modification of an electrolyte matrix material.

With the above and other objects in view, a feature of the invention is the provision of hematin derivatized with one or more non-proteinaceous amphipathic groups, wherein the preferred amphipathic group is polyethylene glycol, and the hematin derivatized is soluble over a pH range of about pH 0.5 to about pH 12.

In accordance with a further feature of the invention, there is provided a method for preparing a derivatized hematin by reacting hematin with an amphipathic compound. In a preferred embodiment, the hematin is derivatized with an amphipathic compound in the presence of a carboxylic acid activating compound for an aprotic base.

In accordance with a still further feature of the invention, there is provided an assembled hematin, which includes alternating layers of hematin and a polyelectrolyte on an electrically charged substrate. Preferably, the polyelectrolyte is cationic.

In another embodiment, the invention includes a method of forming assembled hematin, by alternately depositing one or more layers of hematin and one or more layers of a polyelectrolyte on an electrically charged substrate.

In accordance with another feature of the invention, there is provided a method of polymerizing aromatic monomers, such as

anilines or phenols. In a preferred embodiment, the polymerization takes place in the presence of a template. Typically, the template is anionic.

In accordance with a still further feature of the invention, there is provided a method of polymerizing aromatic monomers by contacting an aromatic monomer and a template with an assembled hematin. Preferably, the aromatic monomer is an aniline or a phenol.

In accordance with still another feature of the invention, there is provided a method of polymerizing an aromatic monomer, which includes combining the aromatic monomer with a derivatized hematin catalyst. In a preferred embodiment, the hematin is derivatized with polyethylene glycoat (PEG). In another preferred embodiment, the derivatized hematin catalyst and the aromatic monomer are additionally combined with a peroxide to initiate the reaction.

Advantages of the present invention include resolving the current limitations of catalysts used in the commercial synthesis of polyaromatic polymers, by reducing the cost of catalyst and by providing a catalyst that is active and stable over a wide range of pHs. The derivatized hematins of the present invention are water-soluble and recyclable, virtually eliminating the need for toxic reagents and solvents, and thus creating an environmentally friendly synthesis for polyaromatic polymers. In addition, the derivatized hematins of the present invention, in combination with

a template, reduce the amount of branching during polymerization, leading to structurally more consistent product.

The present invention is further directed to a syn-enzymatic polymerization process of PYR and/or EDOT in the presence of SPS, which results in a novel complex of PPYR and/or PEDOT with SPS, which has exceptional stability, and good processability.

There have been attempts to use different forms of hematin for catalysis, but it was seen that the catalytic activity was incomparably lower than that of the enzyme. It is known to provide for the efficient synthesis of polyaromatic compounds catalyzed by hematin in mixed solvent systems or buffer systems of high pH values. It has been found suitable to use a chemically modified hematin to effectively synthesize conducting polyaniline in the presence of polyelectrolye templates. Work in this area has attempted to manipulate this artificial catalyst towards the synthesis of conducting PEDOT or PPYR, with the ultimate goal of expanding the versatility of this hydroxy ferriprotoporphyrin based catalyst. The method described herein enables the synthesis of such electroactive polymers, suitable for conductive transparent coatings.

In accordance with a still further feature of the invention, there is provided a unique template assisted approach for the synthesis of water-soluble polymers, involving enzymatic polymerization of aniline and phenol with HRP as the catalyst in the presence of an anionic polyelectrolyte. In this case, the

polyelectrolyte, such as SPS, serves three main functions, namely, to electrostatically align the aniline monomers to promote a para directed approach, to provide counterions for doping the polymer, and to maintain water solubility. Aside from the polyelectrolyte macromolecular templates, micellar templates like sodium dodecylbenzene sulphonic acid, and biological templates, like DNA, have been investigated and seen to be successful nano-reactors in the one-pot enzymatic synthesis of conducting polyanilines. Thus, the template provided an environment wherein the pH and the charge density near the template molecule were different from those of the bulk solution, the polymerization being carried out at pH 4.0, (peroxidases are active in the pH range of 4.0 - 8.0).

In accordance with still another feature of the invention, there is provided a novel synthesis of water soluble PEDOT and PPYR using polyethylene glycoated (PEG) hematin as an efficient catalyst in the presence of SPS as a template. EDOT and PYR have been copolymerized using this unique catalyst.

The above and other features of the invention, including various novel details of construction and combinations of steps, will now be more particularly described with reference to the accompanying drawings and pointed out in the claims. It will be understood that the particular methods embodying the invention are described by way of illustration only and not as limitations of the invention. The principles and features of this invention may

be employed in various and numerous embodiments without departing from the scope of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Reference is made to the accompanying drawings in which are shown illustrative embodiments of the invention, from which its novel features and advantages will be apparent.

In the drawings:

FIG. 1 shows the functionalization of hematin with polyethylene glycol (PEG) in the presence of N,N'-carbonyl diimidazole, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and dimethylformamide (DMF);

FIG. 2 shows the Fourier Transform Infrared (FTIR) spectra of hematin and PEG-hematin. The inset shows an expanded region between 1500 and 1700cm^{-1};

FIG. 3a shows the ^{1}H NMR spectra of hematin and PEG-hematin in DMF-d_7. The inset shows the disappearance of the hematin carboxylic acid peak when it is derivatized with PEG;

FIG. 3b shows the ^{1}H NMR spectra of hematin and PEG-hematin in D_2O;

FIG. 4 shows the catalytic activity of hematin and PEG-hematin for the oxidation of pyrogallol at pH 4.0;

FIG. 5 shows the UV-vis absorption spectrum of aniline monomers and of polyaniline formed during PEG-hematin catalyzed polymerization;

FIG. 6 shows the time dependent UV-vis absorption spectra of the polyaniline-sodium polystyrene sulfonate (SPS) complex formed at pH 4 over 2 hours after initiation of polymerization;

FIG. 7 shows the pH-dependent UV-vis absorption spectra of the polyaniline-SPS complex formed after initiation of polymerization;

FIG. 8 shows the UV-vis absorption spectra of polyaniline-SPS complex as it is titrated with 1 N NaOH and 1 N HCl, demonstrating that the complex can be reversibly depoded and redoped using base or acid, respectively;

FIG. 9 shows a cycle voltammogram of a solution cast film of polyaniline-SPS complex synthesized at pH 1.0;

FIG. 10 shows the pH-dependent UV-vis absorption spectra of polyaniline-lignin sulfonate complexes formed during polymerization;

FIG. 11 shows UV-vis absorption spectra of polyaniline-DNA formed during PEG-hematin catalyzed polymerization;

FIG. 12 shows CD spectra of polyaniline-DNA formed during PEG-hematin catalyzed polymerization;

FIG. 13 shows time-dependent UV-vis absorption spectra of the polymerization of 2-methoxy-5-methylaniline catalyzed by PEG-hematin;

FIG. 14 shows pH-dependent UV-vis absorption spectra of polyaniline-dodecylbenzenesulfonic acid complexes formed during polymerization;

FIG. 15 shows UV-vis absorption spectra of a SPS-polyphenol complex formed during polymerization;

FIG. 16 is an ultra-violet spectrum of PEDOT templated on SPS at pH 1.0, 11.0 synthesized using PEG-Hematin;

FIG. 17 is an FTIR spectrum of EDOT and SPS-PEDOT collected after polymerization;

FIG. 18 shows an ultra-violet spectra of PYR and PPYR templated on SPS at pH 2.0, after polymerization thereof;

FIG. 19 shows an FTIR spectra of the polymers PYR and PPYR; and

FIG. 20 shows ultra violet spectra of the copolymer of PEDOT and PPYR templated on SPS, and of the native PYR.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention generally includes a derivatized hematin and an assembled hematin, along with methods of preparing the hematins. The invention also includes methods of polymerizing aromatic monomers in a reaction catalyzed by an assembled hematin or a derivatized hematin.

The methods of the present invention include the use of hematin, a hydroxyferriprotoporphyrin, which has been derivatized with one or more non-proteinaceous amphipathic groups. Examples of amphipathic groups include phosphoglycerides, sphingomyelin, glycolipids, substituted or unsubstituted polyethers and polyalkylene glycols, substituted or unsubstituted polyamines such

as polyethyleneimine, polyallylamine, and poly(diallylamine); polyammonium groups, such as poly(allylammonium salts), poly(trimethylallylammonium salts), poly(triethyallylammonium salts), poly(dimethyldiallylammonium salts), poly(diethyldiallylammonium salts), and polysaccharides such as hydroxypropyl cellulose, hydroxymethyl cellulose, and hydroxyethyl cellulose.

Preferred amphipathic groups include polyalkylene glycols, such as polyethylene glycol and polypropylene glycol. Preferably, polyethylene glycol groups have a molecular weight of about 400 to about 100,000, or more, and preferably a molecular weight of about 5,000 to about 15,000.

Aromatic monomers include substituted and unsubstituted aromatic compounds. Suitable aromatic compounds include 4-(p-hydroxyphenylazo)pyridine and 4-(p-hydroxyphenylazo)pyridinium methiodide. Preferred aromatic compounds for polymerization include aniline, phenol, and 2-methoxy-5-methylaniline.

Suitable substituents on aromatic monomers will not significantly reduce the rate of polymerization as compared to an unsubstituted aromatic monomer (e.g., will not reduce the rate of polymerization by more than ten-fold). Examples of suitable substituents for aromatic monomers include, for example, halogen (-Br, -Cl, -I, and -F), -OR, -CN, $-NO_2$, -COOR, $-CONRR_1$, $-SO_kR$ (where k is 0, 1, or 2), $-NRR_1$, -SR, haloalkyl groups, and -NH-C(=NH)-NH_2. R and R_1 are independently, -H, an aliphatic group,

and aralkyl group, a heteroaralkyl group, and aromatic group, or a substituted aromatic group. A substituted aromatic monomer can have more than one substituent.

In a preferred embodiment of the present invention, a template is combined with the derivatized hematin, an aromatic monomer, and a peroxide, such that the aromatic monomer aligns along the template and polymerizes to form a complex including the polymerized aromatic monomer and the template. A "template," as that term is employed herein, refers to a polymer or oligomer that can bind, such as ionically bind, to the aromatic monomer being polymerized.

Suitable template polymers include polyelectrolytes, such as an anionic polymer or a cationic polymer. Anionic polymer templates include polymers that include pendant acid functional groups such as poly(vinylbenzoic acid) and salts thereof, poly(vinyl polyphosphonic acid) and salts thereof, poly(glutamic acid) and salts thereof, poly(aspartic acid) and salts thereof, poly(acrylic acid), and poly(maleic acid co-olefin) and salts thereof. Co-olefins that can be polymerized with maleic acid to form poly(maleic acid co-olefin) include 1-propene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, and 1-decene. Preferred anionic polymer templates include poly(styrene sulfonic acid) and salts thereof, lignin sulfonic acid and salts thereof, and dodecylbenzene sulfonic acid and salts thereof.

Optically active templates can be employed in the polymerization method of the invention. When an optically active template is employed, the template can induce macro-asymmetry in the polymerized aromatic monomer due to the close association of the template with the polymerized aromatic monomer in the complex. Examples of optically active templates include polynucleic acids and salts thereof, such as rubonucleic acids and 2'-deoxyribonucleic acids. Other suitable templates include biological receptors, peptides, proteins, zeolites, caged compounds, phenol red, azo compounds, azo polymers, and dendrimers.

In a preferred embodiment, the complex of a polymerized aromatic monomer and a template is a water-soluble complex of a polyaniline and a template. Preferably, the polyaniline (pani) is of the electrically-conducting emeraldine salt form. Emaraldine is an electrically-conducting form of pani, and has a characteristic green color when protonated, or doped.

In another preferred embodiment, the complex including a polymerized aromatic monomer and a template is a water-soluble complex of a polyphenol and a template.

In still another preferred embodiment, a polymerized aromatic monomer complexed to an optically active template has a macro-asymmetry.

A complex of a polymerized aromatic monomer and a template is prepared by contacting an aromatic monomer, such as an aniline or

a phenol, and a template with a derivatized hematin in a solution of a pH from about 0 to about 12. Preferably, the solution is buffered, and the pH ranges from about 0 to about 7, and more preferably ranges from about pH 0 to about pH 4. The ratio of aromatic monomer to template (measured as the concentration of template repeat units) can vary from 5:1 to 1:5 (aromatic monomer : template repeat unit), and is preferably from about 2:1 to about 1:2, and is even more preferably about 1:1.

A catalytic amount of the derivatized hematin can be added to the reaction mixture either before or after addition of the aromatic monomer. A catalytic amount of the derivatized hematin is typically between about one unit/mL and five units/mL, where one unit will form 1.0 mg purpurogallin from pyrogallol in 20 seconds at pH6.0 at 20°C. Preferably, the derivatized hematin is added to the solution after addition of the template and aromatic monomer.

In a preferred embodiment, a peroxide is also added to the reaction mixture. The peroxide is added incrementally, such as not to de-activate the derivatized hematin catalyst, until and amount approximately stoichiometric with the amount of aromatic monomer has been added. The reaction can be monitored spectroscopically.

The above polymerization can be carried out in polar solvents such as ethanol, methanol, isopropanol, dimethylformamide,

dioxane, acetonitrile, and diethyl ether, but is preferably carried out in water.

In one embodiment, the present invention is a method of derivatizing hematin, which includes reacting hematin with one or more amphipathic compounds, thereby forming a derivatized hematin. In a preferred embodiment, the hematin is reacted with one or more amphipathic compounds in the presence of a carboxylic acid activating compound and an aprotic base. In a more preferable embodiment, the carboxylic acid activating compound is a dialkylcarbodiimide. In another preferred embodiment, the amphipathic compound is a substituted or unsubstituted polyalkylene glycol. Even more preferably, the polyalkylene glycol is polythylene glycol.

"Carboxylic acid activating compounds," as used in the present description, are compounds that serve to couple a nucleophile, such as a hydroxyl, amine, or thiol group, to a carboxylic acid, thereby forming an ester, an amide, or a thioester linkage. Suitable carboxylic acid activating compounds include dialkylcarbodiimides, preferably diisopropylcarbodiimide and dicyclohexylcarbodiimide; N,N'-carbonyldiimidazole; nitrophenol, preferably o-nitrophenol and p-nitrophenol; pentahalophenol, preferably pentachlorophenol, and pentabromophenol; N-hydroxysuccinimide; tosyl chloride; 1-hydroxybenzotriazole; and N-ethyl-N'-(3-dimethylaminopropyl) carbodiimide.

"Aprotic bases," as used herein, include bases without an exchangeable proton. Suitable aprotic bases include trialkylamines, such as trimethylamine,triethylamine, diisopropylethylamine and triphenylamine; pyridine; pyrimidine; 1,8-diazabicyclo[5.4.0]undec-7-3n3 (DBU); and 1,3,5-triazine.

Derivatized hematins of the present invention can be prepared, for example, by reacting about one-half to about ten mole equivalents of an amphipathic compound, such as polyethylene glycol, with hematin in the presence of an excess of a carboxylic acid activating compound, and an aprotic base, in an aprotic solvent such as dimethylformamide or an ether. The mixture is allowed to stir for about 6 hours to about 6 days, and is then quenched with a large volume of water or other protic solvent. The unreacted reagents are removed by extraction of the reaction mixture with an organic solvent such as ethyl acetate. The water layer is concentrated, preferably by lyophilization, to yield the derivatized hematin.

In another embodiment, the present invention is assembled hematin, which includes one or more layers of hematin alternating with one or more layers of a polyelectrolyte deposited on a substrate. In a preferred embodiment, polyelectrolyte is a cationic polymer, such as a poly(dialkyldiallylammonium salt) or a poly(trialkylallylammonium salt). Preferably, the polyelectrolyte is poly(dimethyldiallylammonium chloride).

In another embodiment, the present invention includes a method of polymerizing an aromatic monomer to form a complex of a polymerized aromatic monomer and a template, by contacting the aromatic monomer and the template with the assembled hematin. Preferably, the template is an anionic polymer, such as poly(styrene sulfonic acid) or a salt thereof. In another preferred embodiment, the aromatic monomer is a substituted or unsubstituted aromatic compound, such as an aniline or a phenol. In yet another preferred embodiment, the complex of the polymerized aromatic monomer and the template forms in solution or the complex forms on the assembled hematin. The complex forming on the assembled hematin can contact one or more layers of hematin or the polyelectrolyte.

In another embodiment, the present invention includes a method of forming assembled hematin, by alternately depositing layers of hematin and a polyelectrolyte onto an electrically charged substrate. Preferably, the polyelectrolyte is a cationic polymer, and more preferably is a poly(dialkyldiallylammonium salt) or a (trialkylallylammonium salt, such as poly (dimethyldiallylammonium chloride).

Assembled hematins of the present invention can be prepared, for example, by dipping a charged substrate, such as a negatively-charged hydrophilized glass slide, into about 0.1 mM to about 100 mM hematin having a pH from about 6 to about 12 at about 0°C to about 50°C for about 1 minute to about 100 minutes. The substrate

is washed with deionized water and dried with a stream of gas, such as nitrogen or argon. The substrate with a single layer of hematin is dipped into about 0.1 mM to about 100 mM polyelectrolyte having a pH from about 6 to about 12 at about 0°C to about 50°C for about 1 minute to about 100 minutes. The substrate is washed with deionized water and dried from a stream of gas, such as nitrogen or argon. The process can then be repeated, from about 1 to about 100 times, to produce multiple alternating layers (or bilayers) of hematin and the polyelectrolyte on the substrate. For a positively-charged substrate, the order of dipping into hematin and a polyelectrolyte is reversed.

Polymerizations catalyzed by assembled hematins of the present invention can be carried out, for example, in a buffered solution, ranging from about pH 1 to about pH 12, at about 0°C to about 50°C. An aromatic monomer and a template are added to the buffered solution, such that the ratio of aromatic monomer to template repeat unit is about 5 to 1 to about 1 to 5. The concentration of aromatic monomer is about 0.01 M to about 1 M. A quantity of assembled hematin, including about 2 to about 100 bilayers of hematin and polyelectrolyte, is added to the solution. A solution of a peroxide, in an amount sufficient to polymerize the aromatic monomer, is added dropwise over about 5 minutes to about 200 minutes. The reaction is maintained for about 1 hour to

about 200 hours. The progress of the reaction can be monitored spectrophotometrically.

A peroxide, as used in the present invention, is an organic or inorganic compound that includes a -O-O- bond, such as ROOR, where R is as defined above. Preferably, one R is hydrogen, to give ROOH. Even more preferably, the peroxide is hydrogen peroxide, HOOH.

Suitable substrates for assembled hematin are any solids that can maintain an electrical charge. Examples of substrates include glasses (e.g., pyrex and glass slides), plastics (e.g., poly(finyl chloride) and poly(ethylene)), ceramics, metals, and the like. Preferred substrates are glass slides, which have been hydrophilized with an aqueous alkali solution, such as Chem-solv, under ultrasonication.

The functionalities of the polymers may be tuned to impart requisites, such as sensing, electrochemical, optical and electronic properties through copolymerization with functionalized monomers. The polymers have sites for further modifications, such as covalently coupling other functionalities and even biomolecules through simple coupling chemistry.

The conducting polymers in these polymer complexes will allow for use in a wide range of applications including, but not limited to, chemical and biological sensing, electrostatic shielding, photovoltaic cell corrosion protection, light rechargeable batteries, flexible light-emitting diodes, electrochromic devices,

smart windows, chaff materials, electromagnetic radiation absorbers and modulaters, and drug delivery systems.

Accordingly, to achieve the foregoing objects and in accordance with the purpose of the invention, as embodied and broadly described herein, a method for matrix assisted, syn-enzyme-catalyzed polymerization or copolymerization of PYR, PEDOT and aniline comprises the preparation of an aqueous solution containing PYR and/or PEDOT, SPS, Hem-PEG syn-enzyme and a reaction initiator (hydrogen peroxide). The procedure is a one-step, in situ reaction, which is highly selective and which produces minimal by-products and chemical waste. The resulting polymers or copolymers solution can be used immediately as is or purified via such techniques as dialysis and centrifugation.

Matrix materials may include, but are not limited to, electrolytes which have various aromatic backbones and/or pendant groups, aliphatic backbones and/or pendant groups, optically active (chromophoric) backbones and/or pendant groups, electrically active backbones and/or pendant groups and various degrees of sulfonation/functionalization. The ionized groups on these electrolyte matrices may include and are not limited to sulfonates, carboxylates, phosphates, and borates. Manipulation of the molecular weight and purity of the matrices will allow for optimized polymerization and processing conditions.

The present invention is premised on the discovery that unsurpassed electrical and optical stability, processability,

tunability and environmental compatibility are imparted to a new matrix assisted syn-enzymatic polymerization of EDOT, pyrrole, aniline and phenol. In addition, with judicious choice of matrix and/or monomer, the final polymer complex properties may be tailored to suit a wide range of real device applications.

The present invention will now be further described by the following non-limiting examples.

EXAMPLE 1

Synthesis of PEG-Hematin complex

The PEG-hematin complex was obtained through the coupling of PEG chains to a hematin molecule through ester linkages as shown in FIG. 1. The PEG-hematin complex was prepared by the addition of a mole equivalent of PEG (19 mg) to hematin (200 mg) in the presence of activators N, N'-carbonyldiimidazole (0.05 g) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.047 g) in DMF. The mixture was allowed to stir for 48 hours then was quenched by the addition of a large volume of deionized water. The unreacted reagents were removed by extraction with ethyl acetate. The water layer was subsequently lyophilized to yield PEG-hematin as a reddish-brown solid.

The complex was characterized using NMR and FTIR spectroscopy. The average extent of modification of the acidic groups of hematin was determined using UV-vis spectroscopy. The UV-vis spectra of the PEG-hematin exhibited a decrease in the

Soret band (420 nm), a porphyrin centered π-π^* transition, in comparison to hematin, which was used to calculate the amount of hematin present in the sample. However, the energy and spectral bandwidths of PEG-hematin were indistinguishable from hematin, which indicated that the modification of hematin by poly (ethylene glycol) does not affect the heme structure. Based on this assumption, the average concentration of hematin in the PEG-hematin sample was subsequently determined to be 67% by weight.

An FTIR spectrum of PEG-hematin indicated the presence of an ester functionality by the appearance of a doublet at 1646 and 1651 cm^{-1} (similar to diethyl phthalate) accompanied by the complete disappearance of the peak at 1712 cm^{-1} for the acid carbonyl of hematin (FIG. 2). The strong peak at 1100 cm^{-1} corresponded to the ether linkage of the glycol moiety.

An ^1H NMR spectrum of PEG-hematin in DMF-d_7 shows the disappearance of the peak at 10.2 ppm, which was assigned to the carboxylic proton of hematin (FIG. 3a). This clearly indicated that the carboxylic acid hydroxyl moiety was transformed into an ester. The large broad peak at 3.8 ppm was assigned to the poly (ethylene glycol) protons. However, the spectra could not be well resolved in the region of 2-4 ppm due to the interference of the peaks assigned to the residual protons in deuterated DMF. In order to get a better resolution of the spectrum, the solvent system was changed to deuterated water. The spectrum D_2O could not be used to distinguish the absence of the carboxylic acid

proton due to proton exchange with D_2O. However, comparison of the spectrum of PEG-hematin and spectrum of poly(ethylene glycol), in D_2O showed the changes in the position of the PEG peaks of PEG-hematin in comparison to PEG alone. It was found the PEG exhibited a major peak at 3.8 ppm, which was assigned to the bulk of the polymer chains, while the adjoining peaks (triplets) were assigned to the end groups of the polymer. When a PEG-hematin derivative was formed, the peak at 4.0 ppm shifted upfield and merged into the main peak. This was accompanied by considerable broadening and a shift of the peak at 3.8 ppm to 3.6 ppm (FIG. 3b). It was postulated that methylene protons α to the hydroxy group PEG, on being attached by an ester linkage to hematin, shifted upfield while methylene protons β to the hydroxy groups of PEG were affected by the inhomogeneous paramagnetic environment, leading to broadening. These observed changes strongly indicated the formation of an ester bond between PEG and hematin.

The activity of the PEG-hematin was assessed through the oxidation of pyrogallo (0.5%) to purpurogallin in 14 mM potassium phosphate buffer in the presence of 0.027% (w/w) hydrogen peroxide. The activity of the PEG-hematin was found to be approximately 30-fold higher as compared to native hematin at a pH 4.0 (FIG. 4). It is believed that the activity of hematin is dependent on its solubility. Thus, the enhanced activity of the PEG-hematin is attributed to its enhanced solubility.

EXAMPLE 2

Synthesis of Polyanine (Pani)

The polymerization of aniline was carried out in 0.1 M sodium phosphate buffer (10 mL) maintained at pH 1. To this buffer solution the aniline monomer was added. The catalyst, PEG-hematin (60 μg), was added only just prior to the addition of hydrogen peroxide. The polymerizatrion was initiated by the incremental addition of a stoichiometric amount of hydrogen peroxide, with respect to aniline. 0.3% H_2O_2 (w/v) was used with constant stirring and the progress of the reaction was monitored spectroscopically (FIG. 5). Typically, all reaction systems were left stirred until completion of polymerization followed by precipitation of the pani. The pani synthesized was filtered off and thoroughly washed with acetone a few times followed by drying in a vacuum oven. The conductivity of the pani pellet was found to be of the order of 0.2 S/cm.

This reaction thus proved the versatility and ability of the PEG-Hematin for the synthesis of stable conducting pani even in the absence of template. The pani formed in this case was again redox reversible as proved by cyclic voltammetry studies.

EXAMPLE 3

Synthesis of Sodium Poly (sodium-4-styrenesulfonate)-Polyaniline Complex

The polymerization of aniline was carried out in 0.1 M sodium phosphate buffer over a range of pH conditions from pH 1-4. A 17 mM solution of SPS template in phosphate buffer (100mM) was prepared to which the aniline monomer was added in a 1:1 molar ratio of aniline to sodium styrene sulfonate monomer. The catalyst, PEG-hematin (5 mg), was added just prior to the addition of hydrogen peroxide. The polymerization was initiated by the incremental addition of a stoichiometric amount of hydrogen peroxide (relative to aniline). In all cases, 0.3% H_2O_2 (w/v) was used with constant stirring, and the progress of the reaction was monitored spectroscopically. On completion of polymerization, the solution was transferred to individual regenerated natural cellulose membrane bags (molecular weight cut-off 10,000 D) and were dialyzed against 5000 mL of acidified deionized water maintained at pH 4.0 to remove unreacted monomers and oligomers. The solid SPS-Pani complex was obtained by evaporation of the deionized water followed by drying in a vacuum oven.

It was observed that the solution slowly turned dark green, indicating the formation of the doped emeraldine salt form of conducting pani. The UV-vis absorption spectra of the Pani/SPS complex, formed at different time intervals over a period of 2 hours at pH 4.0 after initiation of polymerization reaction, is shown in FIG. 6. The UV-vis spectra showed the presence of polaron absorption bands at 400 nm and 800-1200 nm, which was consistent with the formation of the conducting form of pani.

This polymerization was also carried out at different pH values ranging from pH 1.0 to pH 4.0 as shown in FIG. 7. The formation of pani was observed in all cases, thus demonstrating the stability and robustness of the PEG-hematin in comparison to hematin (insoluble at low pH) or horseradish peroxidase, HRP (denatured at low pH). Also, the pani formation reaction catalyzed by PEG-hematin was found to be complete with greater than 90% yield within a few hours, while the unmodified hematin showed little or no reactivity within the same time period under these acidic conditions.

The redox tunability of the pani formed was further demonstrated by dedoping the emaraldine salt form of pani at high pH and then redoping with acid. With increasing pH (dedoping) on titration with 1 N NaOH, the polaron bands at 400 nm and 8(0nm were found to diminish, while a new band at 600 nm began to emerge due to the exciton transition of the quinoid ring giving rise to a blue solution indicating that the pani had been fully dedoped to the base form. On titrating the solution back with 1 N HCl (redoping), a reversible color change was observed and the spectra is shown in FIG. 8. Furthermore, an isosbestic point at 710 nm was also observed, which was indicative of the changes in the pani oxidation state. This behavior was similar to the pani synthesized chemically or enzymatically with HRP and confirmed the formation of the conducting pani emeraldine salt form (electroactive form) catalyzed by PEG-hematin.

The conductivity of the emeraldine salt form of pani synthesized at pH less than 4 was found to be about 10^{-3} S/cm.

Furthermore, cyclic voltammetry studies were carried out to determine the electrochemical nature of pani synthesized by the PEG-hematin catalysis. The cyclic voltammogram of a cast film of an SPS-pani complex (FIG. 9) showed two sets of peaks indicating two reversible redox cycles at a scan rate of 100 mV/s over a potential window of -0.2-1.2V.

EXAMPLE 4

Synthesis of Lignosulfonate-pani Complex

5.2 mg of a lignin sulfonate polyelectrote complex was dissolved in 10 mL of sodium monophosphate buffer (0.1 M) maintained at pH 4.0. This was followed by the addition of 18 μL of aniline, a catalytic amount of PEG-Hematin and an amount of hydrogen peroxide (0.3%) stoichiometric with aniline. The reaction mixture was allowed to stir until precipitation of the polyelectrolyte-pani complex ceased. The reaction was also carried out in solutions having pHs ranging from pH 1-4 (FIG. 10). The precipitated lignin sulfonate-pani complex obtained was washed several times with acidified acetone to remove the unreacted monomer and finally washed with acidified deionized water, filtered under suction through a polycarbonate filter and dried in a vacuum oven to yield lignin sulfonate pani complex.

When the polymerization was conducted at pH 3.0, there was a peak of low intensity at 767 nm for the emeraldine form of pani, which was completely absent during polymerization at pH 4.0. The extended absorption of 1200 nm indicated the formation of the extended conjugation of the pani backbone. Thus, the synthesis of pani complexed with a natural polymer further widens the scope of applications to other natural polyelectrolytes to form versatile, environmentally benign conducting polymers.

EXAMPLE 5

Synthesis of DNA-pani Complex

The polymerization of aniline in the presence of Calf Thymus DNA was carried out in sterile 10 mM phosphate buffer. A 1.0 mM calf thymus DNA solution was prepared by dissolving the required amount of DNA in 10 mL of sterilized sodium phosphate buffer maintained at pH 4. The concentration of DNA was determined by the UV absorbance at 258 nm. To this DNA solution, 4.5 µl (5 mM) of aniline was added. The pH of the solution was again checked and adjusted to 4.3, and 5 mg of PEG-Hematin were added. To this reaction mixture, a solution of hydrogen peroxide (0.3% solution, 4.5 µl, 5 mM) was added drop-wise, to initiate the polymerization and reaction of aniline was followed using UV-Vis spectroscopy and circular dichroism polarimetry.

When the aniline monomer was added to a DNA solution at pH 4.3, the electrostatic interaction between the protonated aniline

monomers and the phosphate groups in the DNA caused the monomers to closely associate with the DNA. The association of the protonated aniline monomer on the DNA template facilitated a predominantly *para*-directed coupling and inhibited parasitic branching during the polymerization. The high proton concentration around the phosphate groups also provided a unique local lower pH environment that permitted the polymerization of aniline at a higher pH than that necessary with conventional chemical polymerization of aniline. The polymerization was catalyzed by PEG-hematin and initiated by hydrogen peroxide. However, as the polymerization proceeded over a period of time and a critical chain length was attained, the DNA-pani complex precipitated out of solution.

It was concluded that the complex remained soluble as long as there were enough phosphate groups on the DNA available for solvation. As the polymerization proceeded, the preferred molecular interaction between the charged aniline groups and the phosphate groups of DNA caused the growing chain to occupy a majority of these sites leading to the salting out of the DNA-pani complex. The polymerization reaction was followed using UV-vis spectroscopy and circular dichroism polarimetry.

The UV-vis spectra of the DNA-pani complex recorded after initiation of the polymerization are shown in FIG 11. The UV-vis absorbance spectra showed a peak around 260 nm emerging from the absorption of the base pairs of DNA along with polaron absorption

bands at 420 nm and 750 nm, indicating the formation of the conducting emeraldine salt form of pani.

The bases of the nucleic acid have a plane of symmetry and thus are not intrinsically optically active. However, the deoxyribose sugar is asymmetric and since the bases are attached to the anomeric carbon of these sugars, the sugar can induce a circular dichroism in the absorption bands of the bases. These bands may be observed either for the intensely electronically allowed π-π^* transitions, or for the weakly allowed n-π^* transitions because these transitions are magnetically allowed. Also, the π electron systems of the bases make them hydrophobic, so the bases tend to stack in hydrogen-bonding solvents to minimize the π-electron surface area exposed to the solvent. The hydrophobic planes and hydrophilic edges as well as charge-charge interactions cause the bases to stack and the polymer to adopt a helical structure.

Preferential handedness is induced in these helical structures by the intrinsically asymmetric sugars, giving the DNA polymer a whole super asymmetry. The electronic transitions of these chromophoric bases are in close proximity and can thus interact to give well-defined CD spectra. The CD spectrum of the DNA-pani complex showed a reduction in the intensity of the peak at 275 nm (FIG. 12).

This change indicated a polymorphic transition in DNA causing the DNA to change from a loosely wound form to the over-wound

form. The appearance of a positive peak at 450 nm indicated that the helical polyelectrolyte DNA template induces a macroscopic order in the pani that is formed. This result proves the extensive versatility of the PEG-Hematin catalyst with a variety of templates, including delicate biomacromolecules, in providing the optimal catalytic activity for polymerization.

EXAMPLE 6

Synthesis of Poly(2-methoxy-5-methylaniline)-SPS complex

The polymerization of 2-methoxy-5-methylaniline (2M5M) was carried out in 0.1 M sodium phosphate buffer of pH 4.0. A 17 mM SPS template solution, as measured from the concentration of sodium styrene sulfonate monomers, in phosphate buffer (10 mL) was prepared, to which 2M5M (24 mg) was added in the desired (1:1, 2M5M:SPS) molar ratio. The polymerization was initiated after addition of 5 mg of PEG-Hematin, by the incremental addition of an amount of peroxide (0.3% w/v) stoichiometric with 2M5M, with constant stirring. The progress of the reaction was monitored spectroscopically. After the reaction was complete, the solution was dialyzed to remove the unreacted monomers, followed by evaporation to yield a SPS-poly(2M5M) complex.

The UV-vis absorption spectra of the poly(2M5M)/SPS complex formed is shown if FIG. 14. The spectra again showed the presence of a polaron band at 425 nm and extended conjugation in the longer wavelength range indicating the linear conducting form of pani.

This polymer also showed reversible redox tunability similar to that observed for the SPS-Pani complex formed in Example 2. The SPS-poly(2M5M) formed could also be reversibly de-doped on titrating with 1N NaOH and re-doped by back titrating with 1N HCL.

EXAMPLE 7

Synthesis of Sodium Dodecylbenzenesulfonic Acid-Pani Complex

Polymerization of aniline was carried out in 0.1 M sodium at pH 4. A 17 mM solution of dodecylbenzesulfonic acid (DBSA) in phosphate buffer (100 mM) was prepared to which the aniline monomer was added in the desired (1:1, Aniline:DBSA) molar ratio. The catalyst, PEG-Hematin (5 mg), was added just prior to the addition of hydrogen peroxide. The polymerization was initiated by the incremental addition of an amount of hydrogen peroxide stoichiometric to aniline. In all cases, 0.3% H_2O_2 (w/v) was used with constant stirring. The progress of the reaction was monitored spectroscopically.

EXAMPLE 8

Synthesis of SPS-Polyphenol Complex

A polymerization reaction was carried out in 10 mL of aqueous phosphate buffer (100 mM). The pH of the reaction media for the phenol polymerization was maintained at pH 7.0 and equimolar concentrations (17 mM) of SPS, with respect to the concentration of the repeat units, and phenol monomer were added to the buffered

solution, followed by 10 mg of the PEG-hematin. The reaction was initiated by addition of a stoichiometric, with respect to phenol, amount H_2O_2 (30% w/v) in one lot to facilitate the formation of high molecular weight polypenol. The reaction was monitored spectroscopically. A control experiment was also carried out simultaneously in the absence of catalyst. The final products were dialyzed using Centricon concentrators (10,000 Mw cut off, Amicon Inc., Beverly, MA) to remove unreacted monomers. The samples were then dried under vacuum at 50°C and used for further analysis. The yield was calculated to be typically 95% or higher.

The PEG-hematin complex was also found to catalyze the polymerization of phenol at pH 7.0 more efficiently than that compared to the native hematin and peroxidase (FIG. 15). The large broad absorption tail in the region from 300-700 nm conferred the presence of extended conjugation and indicated formation of polyphenol by PEG-hematin reaction. In comparison, the absorption of the hematin-catalyzed reaction was relatively weak. Thus, modification of the hematin with PEG was observed to significantly improve the reactivity to suit the desired reaction conditions leading to the formation of polyphenol.

EXAMPLE 9

Preparation of Assembled Hematin

Glass slides (25 by 75 mm) were hydrophilized with 1% Chem-solv solution in deionized water under ultrasonication for use as

substrates. This treatment generates negative charges on the surface of the slides due to partial hydrolysis. After 3 hours, the slides were ultrasonicated twice in deionized water for 30 minutes before use.

The electrostatic layer-by-layer deposition process was carried out in two steps. Poly (diallyldimethy/ammoniom chloride) (PDAC) (10 mM) and hematin (3 mM) solutions were prepared over a pH range from 5 to 11. In the first step, hydrophilized glass slides were immersed in PDAC solution for 10 minute at room temperature and washed with deionized water for 5 minutes. After the deposition and washing steps, the slides were dried with a stream of nitrogen. In the second step, the substrates with a single layer of PDAC were immersed into the hematin solution for 10 minutes and subsequently washed with deionized water and dried with a stream of nitrogen to produce an assembled hematin, having a bilayer film of PDAC/hematin. This dipping procedure was iterated to build up multilayer films.

EXAMPLE 10

Synthesis of Pani-SPS Complex Using Assembled Hematin

Polymerization of aniline was carried out at room temperature in a 40mL, 0.1M phosphoric acid buffer solution, which contained a 1:1 molar ratio of SPS (MW 1,000,000; moles correspond to quantity of monomers units) to aniline 0.167g (0.81mmol). SPS was added first to the buffered solution, followed by an addition of 2.1mL

of aniline stock solution (0.036mL aniline to 1 mL buffer at pH 1.4) with constant stirring. A seventeen bilayer Hematin/PDAC assembly was immersed in the solution. To initiate aniline polymerization, 11mL of 0.25% H_2O_2 was added dropwise, incrementally, over 30 minutes. The reaction was maintained for 24 hours, and carried out at different pH values (1.0, 2.0, 3.0). The rate of assembled hematin catalyzed polymerization was monitored by a Perkin-Elmer Lamda-9-UV-vis spectrophotometer at room temperature.

EXAMPLE 11

Synthesis of Pyrrole

Pyrrole polymerization in presence of SPS was catalyzed by PEG-Hematin at 25°C using hydrogen peroxide under ambient conditions. 36.8 mg of SPS was dissolved in deionized water (10 ml) at pH 2.0 for the polymerization of pyrrole (0.2 mM). This was followed by the addition of 5 mg of PEG-Hematin to this solution. The polymerization was initiated by the addition of several aliquots of 800µl of 0.03% hydrogen peroxide added in several small increments. The reactants were stirred for 12 hours to complete the polymerization followed by dialysis using Centricon concentrators. The samples were then dried under vacuum at 60°C and used for further analysis. The gravimetric yield was typically 95% higher.

EXAMPLE 12

Synthesis of Poly (3,4)-ethylenedioxythiophene (PEDOT)

PEDOT polymerization in presence of SPS was catalyzed by PEG-Hematin at 25°C using hydrogen peroxide under ambient conditions. 36.8 mg of SPS was dissolved in deionized water (10 ml) at pH 1.0 for the polymerization of PEDOT (concentration 0.2 mM). This was followed by the addition of 5 mg of PEG-Hematin to this solution. The polymerization was initiated by the addition of several aliquots of 800 µl of 0.03% hydrogen peroxide added in several small increments. The reactants were stirred for 12 hours to complete the polymerization followed by dialysis using Centricon concentrators (10,000 cut off). The samples were then dried under vacuum at 60°C and used for further analysis. The gravimetric yield was typically 95% or higher.

EXAMPLE 13

Synthesis of copolomers using Pyrrole and (3,4)-Ethylenedioxythiophene (EDOT) as monomers

Pyrrole (concentration 0.2 mM) and EDOT (0.2 mM) copolymerization in presence of SPS was catalyzed by PEG-Hematin at 25°C using hydrogen peroxide under ambient conditions. 36.8 mg of SPS was dissolved in deionized water (10 ml) at pH 1.0. This was followed by the addition of 5 mg of PEG-Hematin to this solution. The copolymerization was initiated by the addition of

several aliquots of 800 µl of 0.03 % hydrogen peroxide added in several small increments. The reactants were stirred for 12 hours to complete the copolymerization followed by dialysis using Centricon concentrators. The samples were then dried under vacuum at 60°C and used for further analysis. The gravimetric yield was typically 95% or higher.

EXAMPLE 14

Synthesis of copolymeres using Pyrrole and EDOT as monomers

Pyrrole (concentration 0.2 mM) and EDOT (0.2 mM) copolymerization in the presence of SPS was catalyzed by PEG-Hematin at 25°C using hydrogen peroxide under ambient conditions. 36.8 mg of SPS was dissolved in deionized water (10 ml) at pH 2.0. This was followed by the addition of 5 mg of PEG-Hematin to this solution. The copolymerization was initiated by the addition of several aliquots of 800µl of 0.03% hydrogen peroxide added in several small increments. The reactants were stirred for 12 hours to complete the copolymerization followed by dialysis using Centricon concentrators. The samples were then dried under vacuum at 60°C and used for further analysis. The gravimetric yield was typically 95% or higher.

EXAMPLE 15

Synthesis of copolymers using Pyrrole and Aniline as monomers

Pyrrole (concentration 0.2 mM) and aniline (0.2 mM) copolymerization in presence of SPS was catalyzed by PEG-Hematin at 25°C using hydrogen peroxide under ambient conditions. 36.8 mg of SPS was dissolved in deionized water (10 ml) at pH 2.0. This was followed by the addition of 5 mg of PEG-Hematin to this solution. The copolymerization was initiated by the addition of several aliquots of 800µl of 0.03% hydrogen peroxide added in several small increments. The reactants were stirred for 12 hours to complete the polymerization followed by dialysis using Centricon concentrators. The samples were then dried under vacuum at 60°C and used for further analysis. The gravimetric yield was typically 95% or higher.

EXAMPLE 16

Synthesis of copolymears using Aniline and EDOT as monomers

Aniline (concentration 0.2 mM) and EDOT (0.2mM) copolymerization in presence of SPS was catalyzed by PEG-Hematin at 25°C using hydrogen peroxide under ambient conditions. 36.8 mg of SPS was dissolved in deionized water (10 ml) at pH 2.0. This was followed by the addition of 5 mg of PEG-Hematin to this solution. The copolymerization was initiated by the addition of several aliquots of 800µl of 0.03% hydrogen peroxide added in several small increments. The reactants were stirred for 12 hours to complete the copolymerization followed by dialysis using

Centricon concentrators. The samples were then dried under vacuum at 60°C and used for further analysis. The gravimetric yield was typically 95% or higher.

EXAMPLE 17

Synthesis of copolymers using Pyrrole, Aniline and EDOT as monomers

Pyrrole (concentration 0.2 mM), aniline (0.2mM) and EDOT (0.2 mM) copolymerization in presence of SPS was catalyzed by PEG-Hematin at 25°C using hydrogen peroxide under ambient conditions. 36.8 mg of SPS was dissolved in deionized water (10 ml) at pH 2.0. This was followed by the addition of 5 mg of PEG-Hematin to this solution. The copolymerization was initiated by the addition of several aliquots of 800µl of 0.03% hydrogen peroxide added in several small increments. The reactants were stirred for 12 hours to complete the copolymerization followed by dialysis using Centricon concentrators. The samples were then dried under vacuum at 60°C and used for further analysis. The gravimetric yield was typically 95% or higher.

This invention provides a significant advancement over current methods used for the synthesis of a conducting and processable form of polypyrrole and PEDOT. This method addresses and resolves processability and stability problems, which have

limited the commercial use of polypyrrole and PEDOT. The syn-enzymatic synthesis provides a specific, simple and environmentally friendly synthetic approach, while the SPS provides stability and processability. In addition, the SPS/polypyrrole and SPS/PEDOT complex described herein is expected to transition effectively into may established applications where conductivity is desirable.

While this invention has been particularly shown and described with references to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the scope of the invention encompassed by the appended claims.